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**POLYMER-SUPPORTED METAL NANOPARTICLES  
AND METHOD FOR THEIR MANUFACTURE AND USE**

**CROSS REFERENCE TO RELATED APPLICATION**

- 5           This application claims the benefit of the earlier filing date of United States provisional application No. 60/527,233, which is incorporated herein by reference.

**ACKNOWLEDGEMENT OF GOVERNMENT SUPPORT**

- Certain disclosed embodiments were developed, at least in part, using Federal  
10       Funds provided by NSF EPSCoR: EPS-0132626 and ARO DEPSCoR: DAAD19-01-1-0458 grants. The United States government may have rights in the claimed invention.

**BACKGROUND**

- There has been much interest recently in synthesizing nanometer-sized metal  
15       particles because of their potential applications as new catalysts for organic reactions. See, H. Ohde, C. M. Wai, H. Kim, J. Kim and M. Ohde, *J Am. Chem. Soc.*, 2002, 124, 45400; Y. Niu, L. K. Yeung and R. M. Crooks, *J. Am. Chem. Soc.*, 2001, 123, 6840; and A. Henglein, B. G. Ershov and M. Malow, *J. Phys. Chem.*, 1995, 99, 14129. The effect of metal nanoparticle size on catalytic activities is an interesting aspect of the current research. T. K.  
20       Sau, A. Pal and T. Pal, *J. Phys. Chem. B*, 2001, 105, 9266. However, nanometer-sized metal particles are unstable and tend to agglomerate without a suitable support. Different stabilizing approaches for nanoparticles have been reported in the literature, including the use of chemical stabilizers (A. Henglein, *supra*) dendrimers, (Y. Niu, *et al.*, *supra*) polymers (J. Dai and M. L. Bruening, *Nato. Lett.*, 2002, 2, 497) and microemulsions (D. M. de Jesus  
25       and M. Spiro, *Langmuir*, 2000, 16, 4896). Each of these documents is incorporated herein by reference.

- Hydrodechlorination catalyzed by noble metals, such as palladium and rhodium, is a promising technique for removing chlorine atoms from toxic chlorinated compounds. C. A. Marques, M. Selva, P. Tundo, *J. Org. Chem.* 58 (1993) 5256-5260; B. Coq, G. Ferrat, F. Fingueras, *J. Catal.* 101 (1986) 434-445; and Y. Shindler, Y. Matatov-Meytal, M. Sheintuch, *Ind. Eng. Chem. Res.* 40 (2001), 3301-3308. Various heterogeneous [A. Baiker, *Chem. Rev.* 99 (1999) 453-473; and G. G. Cervantes, F. J. Cadete Santos Aires, J. C. Bertolini, *J. Catal.* 214 (2003) 26-32] and homogeneous catalysts [P. G. Jessop, T. Ikariya, R. Noyori, *Nature* 368(17) (1994) 231; P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* 99  
35       (1999) 475-493] using noble metal catalysts have been reported in the literature. Generally speaking, catalytic activity, recyclability and separation of products from the catalyst are

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three important criteria that can be used to evaluate the performance of noble metal catalysts. Nanometer-sized, noble metal particles are known to exhibit high catalytic activities that appear promising for industrial and environmental applications [L. K. Yeung, C. Ted Lee Jr., K. P. Johnston, R. M. Crooks, *Chem. Commun.* (2001) 2290-2291; Y. Li, E. Boone, M. A. El-Sayed, *Langmuir*, 18 (2002) 4921-4925; H. Ohde, C. M. Wai, H. Kim, J. Kim, M. Ohde, *J. Am. Chem. Soc.* 124(17) (2002) 4540-4541]. A number of methods for preparing metal nanoparticles are known in the literature [T. Teranishi, M. Miyake, *Chem. Mater.* 10 (1998) 594-600; A. Henglein, *J. Phys. Chem. B*, 104(29) (2000) 6683-6685; P. S. Shah, J. D. Holmes, R. C. Doty, K. P. Johnston, B. A. Korgel, *J. Am. Chem. Soc.* 122 (2000) 4245-4246; C. Petit, P. Lixon, M. P. Pileni, *J. Phys. Chem.* 97(49) (1993) 12974-12983].

Since metal nanoparticles are generally unstable, exploration of appropriate supports for stabilizing the metal nanoparticles is a key factor for their successful applications in catalysis. In terms of recyclability, heterogeneous catalysts apparently have great advantages over homogeneous catalysts. However, it is well known that metal particles on supports, such as active carbon, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, tend to lose catalytic activity after repeated uses [I. W. C. E. Arends, R. A. Sheldon, *Appl. Catal. A. Gen.* 212 (2001) 175-187; E. J. Beckman, *Environ. Sci. Technol.* 37 (2003) 5289-5296; A. Gampine, D. P. Eymann, *J. Catal.* 179 (1998) 315-325; G. Yuan, M. A. Keane, *Catal. Today* 88 (2003) 27-36; N. Pernicone, M. Cerboni, G. Prelazzi, F. Pinna, G. Fagherazzi, *Catal. Today* 44 (1998) 129-135]. Various factors for deactivation have been studied and reported. Leaching of metals from supports [W. C. E. Arends, *et al.*, and E. J. Beckman, *supra*], poisoning of metal surface with carbonaceous compounds [G. G. Cervantes, *supra*], and HCl/Cl and sulphur A. Gampine, *et al.*; G. Yuan, *et al.* and N. Pernicone, *et al.*, *supra*], sintering [*Id.*] and agglomeration are major factors that limit practical utility of the catalysts.

As a result, a need still exists for nanoparticles supported catalysts that address the limitations associated with known catalysts.

## SUMMARY

A method for making polymer-supported, metal nanoparticles is disclosed. One embodiment of the method comprises providing a polymer support material, contacting the polymer support with an appropriate metal nanoparticle or metal nanoparticle precursor, and contacting the polymer support material and metal or metal precursor with a fluid that swells the polymer support material sufficiently to allow the metal or metal precursor to diffuse into the polymer support material. If a metal nanoparticle precursor comprising a metal in

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an oxidized state is used, then the method also may comprise reducing the metal of the metal precursor to provide a metal nanoparticle. Typically, but not necessarily, the polymer support material is a plastic, with representative plastic materials including polyalkylene polymers, substituted polyalkylene polymers, halogenated polymers, polyesters, or combinations of such materials. Specific examples of suitable polymer support materials include polyethylene, polypropylene, polybutylene, poly(4-methyl-1-pentene), poly(tetrafluoroethylene), perfluoroalkyl-tetrafluoroethylene copolymer, polyimide, polybenzimidazole, and combinations of such materials.

The metal or the metal of the metal nanoparticle precursor can be any of various metals, including the noble metals, with particular examples including palladium, rhodium, platinum, iridium, osmium, gold, nickel, iron or combinations thereof. The metal of the metal nanoparticle can be an alloy or aggregate of two or more different metals. Often, such metals are in an oxidized state greater than zero, and have one or more moieties coupled thereto typically selected from the group consisting of phosphates,  $\beta$ -diketones, phosphine oxides, dithiocarbamates, crown ethers, and combinations thereof. Specific examples of such moieties include, without limitation, tri-*n*-butylphosphate, tri-*n*-octylphosphate, triphenylphosphate, acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, thenoyltrifluoroacetone, heptafluorobutanoylpivaloylmethane, 4, 4-trifluoro-1-(2-thienyl)-1, 3-butanedione, tri-*n*-butylphosphine oxide, tri-*n*-octylphosphine oxide, triphenylphosphine oxide, bis(trifluoroethyl)dithiocarbamate, diethyldithiocarbamate, H-crown, F2-crown, F6-crown, and combinations thereof. Exemplary metal nanoparticle precursors include Pd(hfa)<sub>2</sub> and Rh(acac)<sub>3</sub>.

The fluid can be any fluid that facilitates polymer swelling. Certain embodiments used carbon dioxide, particularly supercritical carbon dioxide. Fluid modifiers, such as lower alkyl alcohols, lower alkyl esters, lower alkyl phosphates, lower alkyl halogenated organic compounds, and combinations thereof, can be used. Specific exemplary fluid modifiers include methanol, ethanol, ethyl acetate, tributyl phosphate, methylene chloride, chloroform and combinations thereof.

When the method involves reducing the metal of the precursor from an oxidized state to a reduced state, reducing agents that are miscible or soluble in the fluid are preferred. Certain embodiments of the process involved reducing a metal of the metal nanoparticle precursor by contacting the metal precursor with hydrogen, often at a pressure greater than ambient and up to a pressure of at least 300 atmospheres.

A method for performing chemical reactions with the metal nanoparticle(s) also is disclosed. For example, the method may involve performing coupling reactions, or

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reducing or oxidizing sites of unsaturation, such as olefins or arenes, or functional groups capable of being reduced or oxidized. A polymer-supported metal nanoparticle and an organic compound are selected. Such materials are then contacted with suitable reagents, such as a reducing agent or an oxidizing agent. The method also may involve contacting materials with a fluid, including supercritical fluids, such as subcritical or supercritical carbon dioxide.

One example of an effective reducing agent is hydrogen, and hydrogen can be introduced at a pressure greater than ambient. As will be understood by a person of ordinary skill in the art, the reduction or oxidation reaction can be conducted at an elevated temperature, such as a temperature between greater than ambient to at least 300 °C.

Disclosed embodiments of the method are effective for reduction of an olefinic moiety or arenes, including halogenated olefins and arenes. Moreover, the organic compound may have an oxygen-bearing functional group, such as a carbonyl group that can be converted to a hydroxyl group, or to a fully saturated carbon; a nitrogen-bearing functional group, such as a nitro group (e.g., nitrobenzene) that can be converted to an amine (e.g., aniline); a halogenated carbon atom that can be dehydrohalogenated to replace the halogen with hydrogen; or combinations of such reactions. Particular examples of arenes, without limitation, include benzene, naphthalene, anthracene, phenanthrene, halogenated benzene, halogenated naphthalene, halogenated anthracene, halogenated phenanthrene, or combinations thereof.

An important benefit provided by certain of the disclosed embodiments is the ability to select desired reaction products. For example, where plural reaction products are produced, relative amounts of the reaction products can be varied by selecting an appropriate metal nanoparticle, polymer support material, or both. Specific examples of representative reactions include: selecting phenol, palladium as the metal nanoparticle, high density polyethylene as the polymer support material, and where cyclohexanone and cyclohexanol are produced in about 78% and 6% yield, respectively; selecting phenol, palladium as the metal nanoparticle, perfluoroalkyl-tetrafluoroethylene copolymer as the polymer support material is, and where cyclohexanone and cyclohexanol are produced in about 62% and 38% yield, respectively; selecting chlorophenol, palladium as the metal nanoparticle, perfluoroalkyl-tetrafluoroethylene copolymer, high density polyethylene, or combinations thereof as the polymer support, with the reduction reaction products including cyclohexanone, cyclohexanol, cyclohexane, phenol and benzene.

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### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates one embodiment of a reactor system for synthesis of metal nanoparticles stabilized in polymeric supports.

FIG. 2 illustrates one embodiment of a reactor system for catalytic hydrodechlorination of chlorinated starting materials using metal nanoparticles stabilized in polymeric supports.

FIG. 3 is a reactor system for catalytic hydrodechlorination of starting material using metal nanoparticles stabilized in polymeric supports.

FIG. 4 provides optical images of HDPE, where image (1) is original HDPE, image (2) is HDPE with  $\text{Pd}(\text{hfa})_2$ , and image (3) is HDPE with palladium nanoparticles.

FIG. 5 is a tunneling electron micrograph of palladium nanoparticles deposited in HDPE (scale bar is 50 nanometers).

FIG. 6 is an NMR spectrum of benzene hydrogenation products using rhodium-supported nanoparticles.

FIG. 7 is an NMR spectrum of products after hydrodechlorination of chlorobenzene using palladium supported nanoparticles.

FIG. 8 is a graph of reaction time versus percent conversion illustrating hydrodechlorination of 2,4-dichlorophenol using palladium-perfluoroalkyl-tetrafluoroethylene copolymer in supercritical carbon dioxide at 50 °C and 100 atmospheres, where ■ is 2,4-dichlorophenol, ▲ is cyclohexanone, □ is cyclohexanol, Δ is cyclohexane, and ○ is phenol.

FIG. 9A is an NMR spectrum of products after hydrodechlorination of 4-chlorobiphenyl using palladium-perfluoroalkyl-tetrafluoroethylene copolymer for 30 minutes at 80 °C, and FIG. 9B is an NMR spectrum of 4-chlorobiphenyl before the hydrodechlorination.

### DETAILED DESCRIPTION

Plastics swell in many fluids, particularly supercritical fluids, such as supercritical  $\text{CO}_2$ . Metal precursors dissolved in the fluid phase can penetrate into these plastic structures. After reduction, if necessary, of the metal precursors, the resulting metals are trapped as nanometer-sized particles and stabilized in the plastic structures. These products or reagents can be used to perform myriad organic reactions.

For example, the reagents can be used to perform reduction reactions, oxidation reactions, coupling reactions, such as the Heck reaction, etc. These reactions are exemplified herein by reduction reactions, such as hydrogen reductions. During catalytic

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hydrogenation, starting materials and reagents, such as hydrogen gas, can penetrate into the swelled plastic structures and diffuse into the interior of the polymer-containing metal nanoparticles. Catalytic hydrogenation therefore occurs effectively. Because the hydrodynamic diameters of metal nanoparticles trapped in the polymer generally are much larger than the starting materials (such as benzene and phenol), the polymer structures allow the reactants to diffuse into the interior but preclude metal nanoparticles from diffusing and agglomerating. Therefore, not only do the metal nanoparticles exist on the surface of the plastic but they also are present in the interior of the polymer and are available for reaction. Consequently, the amount of metal nanoparticles-per-volume of the supporting polymer material can be extremely high compared with those of conventional active carbon- and alumina-supported metal catalysts. Thus, the plastic stabilized metal nanoparticles can be used repeatedly without losing their catalytic capabilities.

After reaction, the products diffuse away from the polymer structure. Finally the products can be easily separated from the polymer catalysts.

Reactions can be facilitated by the using supercritical fluids, such as supercritical carbon dioxide. The supercritical fluid may facilitate reaction by, for example, dissolving one or more starting materials or reagents, dissolving one or more of the byproducts, facilitating entry into the polymer support pores so that contact between reactants occurs efficiently, etc., and combinations of these processes. Moreover, using supercritical fluids can facilitate work-up procedures. For example, byproducts may be separated from desired products by rapid expansion of the supercritical fluid, such as supercritical carbon dioxide.

#### A. Definitions

The following definitions are provided to aid the reader, and are not intended to provide a definition that would be narrower than would be understood by a person of ordinary skill in the art.

Arene – typically unsaturated cyclic hydrocarbons or aliphatic compounds having one or more rings, and including certain heterocyclic compounds. Arenes typically have delocalized  $\Pi$  electrons and satisfy the Huckel  $(4n + 2)$   $\Pi$  electron requirement.

Dehalohydrogenation – replacement of one or more halogen atoms, such as chlorine, by hydrogen atom(s).

Functional group – an atom or group of atoms that defines the structure of a particular family of organic compounds and contributes to their chemical properties. Examples of functional groups include, without limitation, alcohols, aldehydes, alkenes, alkynes, amines, carboxylic acids, epoxides, ethers, ketones, phenols, etc.

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Halogenated – compounds having one or more halogen atoms.

Hydrogenation – any reaction of hydrogen with an organic compound.

Lower alkyl - compounds having ten or fewer carbon atoms, and including both straight-chain and branched-chain compounds and all stereoisomers.

5        Reduce (or reduction) – opposite of oxidize, i.e. a reaction in which electrons are transferred such that the compound receiving electrons is reduced.

Olefin – class of unsaturated aliphatic compounds having one or more double bonds.

10        Oxidize (or oxidation) – a reaction in which electrons are transferred, such that a compound losing electrons is oxidized.

Unsaturation – a state for a compound in which not all of the available valence bonds are satisfied, and in such compounds extra bonds usually form as double or triple bonds.

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#### **B.        Metals**

In general, metals are elements that form positive ions in solution and produce oxides that form hydroxides rather than acids with water. The genus of metals useful for the presently disclosed embodiments includes many species, particularly the noble metals. Noble metals, in general, are metals that are resistant to oxidation. The noble metals include  
20        gold, palladium, platinum, rhodium, iridium, and osmium. The platinum group metals are platinum, palladium, iridium, rhodium, ruthenium and osmium. Transition metals also may be useful for forming polymer-supported, metal nanoparticle reagents and catalysts. Additional particular examples, without limitation, of useful metals include nickel and iron. The present invention is specifically exemplified by formation of palladium and rhodium  
25        polymer supported catalysts, and the use of such metals for performing chemical reactions, such as reduction and dehalogenation reactions.

Suitable metal nanoparticles can be used alone or in combination. Binary, ternary and higher order metallic nanoparticles may provide beneficial results. For example and without limitation, a mixture of Pd and Rh, or a mixture of Pd and Ni, etc. could be  
30        deposited in polymer supports using disclosed. Binary metal catalysts often show synergistic effects that could make the mixed catalysts more active than each individual metal. Mixed metal nanoparticles can be provided in a variety of forms, such as alloys or as aggregates.

### C. *Metal Nanoparticle Precursors*

Certain of the metal nanoparticle polymer-supported reagents or catalysts are made using metal precursors. These materials typically include metals in an oxidation state higher than zero and often include ligands or are chelated with other moieties. For example, disclosed embodiments used palladium (II) hexafluoroacetylacetone and rhodium (III) acetylacetone as metal precursors. The additional moieties may be used for a variety of purposes, such as to facilitate miscibility or solubility of the metal precursor in a fluid of choice, such as high pressure or supercritical gases, including supercritical carbon dioxide. Examples of suitable ligands or chelating agents include, without limitation: phosphates, such as tri-*n*-butylphosphate (TBP), tri-*n*-octylphosphate, and lower alkylphosphates triphenylphosphate;  $\beta$ -diketones, such as acetylacetone (AA or acac), trifluoroacetylacetone (TAA), hexafluoroacetylacetone (HFA), thenoyltrifluoroacetone (TTA), heptafluorobutanoylpivaloylmethane (FOD), and 4, 4-trifluoro-1-(2-thienyl)-1, 3-butanedione (HTTA), phosphine oxides, such as tri-*n*-butylphosphine oxide, tri-*n*-octylphosphine oxide (TOPO), and triphenylphosphine oxide (TPPO); dithiocarbamates, such as bis(trifluoroethyl)dithiocarbamate (FDDC), and diethyldithiocarbamate (DDC); and crown ethers, such as "H-crown" (described in U.S. Pat. No. 5,770,085), "F2-crown" (described in U.S. Pat. No. 5,770,085), and "F6-crown" (described in U.S. Pat. No. 5,770,085).

### D. *Fluids*

In embodiments of the disclosed method, the formation of the metal nanoparticle reagent or catalyst occurs in a fluid and/or a supercritical fluid, most typically in a supercritical fluid. In some embodiments the solvent is a gas at room temperature and atmospheric pressure. A compound exists as a supercritical fluid when it is at a temperature and pressure above a critical temperature and pressure characteristic of the compound. Materials in a supercritical state exhibit properties of both a gas and a liquid. Supercritical fluids typically are able to act as solvents, like subcritical liquids, while also exhibiting the improved penetration power of gases. This makes supercritical fluids a preferred class of fluids for the disclosed embodiments.

Suitable solvents include, but are not limited to, carbon dioxide, nitrogen, nitrous oxide, methane, ethylene, propane, and propylene. Carbon dioxide is a preferred solvent for both subcritical and supercritical fluid reactions. Carbon dioxide has a critical temperature ( $T_c$ ) of 31 °C and a critical pressure ( $P_c$ ) of 73 atmospheres. Supercritical carbon dioxide is

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non-explosive and thoroughly safe for extractions. Carbon dioxide also is a preferred solvent because it is abundantly available and relatively inexpensive.

Carbon dioxide phase diagrams illustrate conditions necessary to produce either subcritical liquid carbon dioxide or supercritical carbon dioxide. Certain conditions above  
5 the critical point produce supercritical carbon dioxide fluids. As an alternative to supercritical carbon dioxide, liquid carbon dioxide is suitable for some embodiments of the disclosed method. At room temperature carbon dioxide becomes a liquid above 5.1 atmospheres. Depending on the pressure, liquid carbon dioxide has a density comparable to or slightly greater than the density of supercritical carbon dioxide. Thus, the solvation  
10 power of liquid carbon dioxide is comparable to or slightly greater than that of supercritical carbon dioxide. But, liquid carbon dioxide does not have the "gas-like" properties of supercritical carbon dioxide. Liquid carbon dioxide has a high viscosity, a low diffusivity, and consequently a poor penetration power compared to supercritical carbon dioxide.

The liquid and supercritical fluid solvents used in embodiments of the disclosed  
15 method may be used individually or in combination. Additional examples of suitable solvents, and their critical temperatures and pressures, are shown in Table 1:

**Table 1**  
**Physical Properties of Selected Supercritical Fluids**

Fluid	Formula	T <sub>c</sub> (°C)	P <sub>c</sub> (atmospheres)
Carbon dioxide	CO <sub>2</sub>	31.1	72.9
Nitrous oxide	N <sub>2</sub> O	36.5	71.7
Ammonia	NH <sub>3</sub>	132.5	112.5
n-Pentane	C <sub>5</sub> H <sub>12</sub>	196.6	33.3
n-Butane	C <sub>4</sub> H <sub>10</sub>	152.0	37.5
n-Propane	C <sub>3</sub> H <sub>6</sub>	96.8	42.0
Sulfur hexafluoride	SF <sub>6</sub>	45.5	37.1
Xenon	Xe	16.6	58.4
Dichlorodifluoromethane	CCl <sub>2</sub> F <sub>2</sub>	111.8	40.7
Trifluoromethane	CHF <sub>3</sub>	25.9	46.9
Methanol	CH <sub>3</sub> OH	240.5	78.9
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	243.4	63.0
Isopropanol	C <sub>3</sub> H <sub>7</sub> OH	235.3	47.0
Diethyl ether	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	193.6	36.3
Water	H <sub>2</sub> O	374.1	218.3

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### *E. Fluid Modifiers*

In some embodiments of the disclosed method, a modifier can be added to the selected fluid to vary the characteristics thereof. For example, a modifier can be added to the selected fluid to enhance the solubility of a particular reagent used or products made by the disclosed embodiments. Some useful modifiers include, without limitation, low-to-  
10 medium boiling point alcohols and esters, such as lower alkyl alcohols and esters; alkyl phosphates, typically lower alkyl phosphates, such as tributylphosphate; and halogenated compounds, such as lower alkyl halogenated organic compounds, including methylene chloride and chloroform. Thus, typical modifiers can be selected from the group consisting of methanol, ethanol, ethyl acetate, tributylphosphate, methylene chloride, chloroform, and  
15 combinations thereof.

The modifiers are added to the solvent in an amount sufficient to vary the characteristics thereof. This can be an amount, for example, between about 0.1% and about 20.0% by weight. The modifiers contemplated for use with embodiments of the disclosed

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method most typically are not supercritical fluids at the disclosed operating conditions. Rather, the modifiers simply are dissolved in the liquid and/or supercritical fluid solvents to improve their solvent properties.

In one embodiment of the disclosed method, a modifier is combined with reagents  
5 prior to introduction into a reaction vessel. Alternatively, the fluid used, such as supercritical carbon dioxide, solvent and the modifier can be added to the reaction vessel separately.

#### *F. Polymeric Supports*

10 Disclosed embodiments of metal nanoparticle chemical reagents, such as catalysts, may be deposited on and in polymeric support materials. Suitable polymeric support materials may be any such materials now known or hereafter developed that allow formation of useful chemical reagents comprising metal nanoparticles. For example, one  
15 consideration is the ability of the polymeric support material to receive metal nanoparticles within polymer pores. Certain fluids, such as supercritical carbon dioxide, facilitate this process by swelling the polymeric material, thereby allowing the metal or metal precursor to diffuse into the polymer pores.

Solely to exemplify the types of polymeric materials useful for the disclosed embodiments, and without limitation, typical polymeric support materials are plastics.  
20 Specific examples of suitable plastics include, again by way of example and without limitation: polyalkylenes, such as polyethylenes, polypropylenes, polybutylenes, etc., and typically high density polyalkylenes, such as high density polyethylene; substituted polyalkylenes, such as poly(4-methyl-1-pentene); halogenated polymers, such as fluoropolymers, including poly(tetrafluoroethylene) and perfluoroalkyl-tetrafluoroethylene  
25 copolymer; polyesters; polyimides; polybenzimidazoles; and combinations of such materials.

Many reactions conducted with the metal nanoparticle polymer supported reagents are facilitated by higher temperatures and/or pressures. Thus, another factor that can be considered for selection of an appropriate polymer support material is its softening or  
30 melting temperature. If the polymer support softens too much, or melts, then the supported metal nanoparticles may be released from the polymer support. Thus, for example, high density polyethylene may be selected, as opposed to low density polyethylene, because high density polyethylene has a higher softening temperature, and hence can be used with reactions facilitated by higher temperatures than can be conducted with low density  
35 polyethylene.

### G. *Reagent and Reaction Apparatus*

FIG. 1 illustrates one embodiment of a system 10 useful for synthesis of metal-polymer supported reagents according to the present invention. In general, such systems include a reaction vessel, a fluid source, and a source of a reducing or oxidizing agent. More specifically, and with reference to FIG. 1, the illustrated system 10 includes a reaction vessel 12, preferably constructed from a resistant material, such as stainless steel. Vessel 12 of FIG. 1 is a 50-milliliter, stainless steel reaction vessel having a fluid inlet port 14 and a fluid outlet port 16. An injection vessel 18 is provided that is fluidly coupled to the inlet port 14 by fluid conduit 20 through an in-line high pressure valve 22. Injection vessel 18 in turn is fluidly coupled to a fluid, such as carbon dioxide, source 24 via fluid conduit and a source 26 of a reducing agent, such as hydrogen. An ISCO syringe pump (not shown) was used to meter to and pressurize fluid in the injection vessel 18. In-line valves 28, 30 and 32 were included to provide fluid flow control to the injection vessel 18. Heating the reactants can facilitate making the metal nanoparticle-plastic support reagents. Therefore, reaction vessel 12 and injection vessel 18 were positioned in an oven 32. Plastic material 34 was placed inside reaction vessel 12, along with a metal or metal precursor.

FIG. 2 illustrates one embodiment 100 of a system useful for performing reactions using metal nanoparticle-plastic supported reagents, such as hydrodechlorination. System 100 includes a reaction vessel 102, preferably constructed from a resistant material, such as stainless steel. Illustrated vessel 102 of FIG. 2 is a 10-milliliter, stainless steel vessel having a fluid inlet port 104 that is fluidly coupled to a fluid, such as carbon dioxide, source 106 via fluid conduit 108 and a source 110 of a reducing agent, such as hydrogen. High-pressure, in-line valves 112, 114, 116 and 118 provide fluid flow control to the vessel 102. A collection vessel 120 was provided as well. Reaction vessel 102 was placed in an oven 122. Plastic material 124 was placed inside reaction vessel 102, along with a metal or metal precursor (not illustrated).

FIG. 3 illustrates one embodiment 200 of a system useful for performing reactions using metal nanoparticle-plastic supported reagents, such as hydrodechlorination. System 200 was used, for example, for hydrodechlorination of 4-chlorobiphenyl. System 200 includes a reaction vessel 202, preferably constructed from a resistant material, such as stainless steel. Illustrated vessel 202 of FIG. 3 is a 15-milliliter, stainless steel vessel having a fluid inlet port 204. System 200 includes a second reactant storage vessel 206 that, for hydrodechlorination of 4-chlorobiphenyl, was used to store the 4-chlorobiphenyl. Vessel 206 in the illustrated embodiment had a capacity of about 40 milliliters. Vessels 202 and

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206 are fluidly coupled via conduit 208 through in-line, high pressure valve 210. Vessel 206 includes ports 212 and 214. Port 212 was fluidly coupled to vessel 202 via fluid conduit 208 through in-line, high pressure valve 216. Port 212 also was fluidly coupled to a reducing agent, such as hydrogen, source 218 through in-line, high pressure valve 220. Port 214 is fluidly coupled to a fluid, such as carbon dioxide, source 222 via fluid conduit 224 through high-pressure, in-line valves 226 and 228. A collection vessel 230 was provided as well. Vessels 202 and 206 were positioned in an oven 232. Metal nanoparticle-polymer support reagents, such as perfluoroalkyl-tetrafluoroethylene copolymer-palladium, are placed in reaction vessel 202.

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### EXAMPLES

The following examples are provided to illustrate particular features of working embodiments. A person of ordinary skill in the art will recognize that the scope of the invention is not limited to the particular features recited in these examples.

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#### EXAMPLE 1

This example describes a method for making plastic-supported metal nanoparticles. Plastic-supported palladium and rhodium nanoparticles were prepared by hydrogen reduction of Pd(II) hexafluoroacetylacetonate [Pd(hfa)<sub>2</sub>] and Rh(III) acetylacetonate [Rh(acac)<sub>3</sub>] in supercritical CO<sub>2</sub>. Watkins and McCarthy previously reported that nanometer-sized platinum particles could be uniformly deposited into poly(4-methyl-1-pentene) and poly(tetrafluoroethylene) in supercritical CO<sub>2</sub> by hydrogen reduction of a platinum precursor. J. J. Watkins and T. J. McCarthy, *Chem. Mater.*, 1995, 7, 1991, incorporated herein by reference. A 50-mL, high-pressure, stainless, flat-bottom cell was used for the synthesis of the metal nanoparticles. High density polyethylene (HDPE) granules (3 mm diameter) and fluoropolymer (PFA) tube (6 mm diameter) obtained from Aldrich were used as supporting plastics. The PFA tubing was sliced into rings with a 1 mm width. The plastic materials were placed in a 50 mL high-pressure cell together with 250 mg of the metal precursor [Pd(hfa)<sub>2</sub> or Rh(acac)<sub>3</sub>]. The 50 mL cell was then pressurized by 100 atmospheres CO<sub>2</sub> to dissolve the Pd or Rh precursor in supercritical CO<sub>2</sub>. Hydrogen gas (10 atmospheres) was introduced into a separate injection vessel (10 mL volume) followed by pressurizing the injection vessel with 200 atmospheres CO<sub>2</sub>. Hydrogen was injected into the 50-mL, high pressure cell with the aid of the pressure difference between the two cells by opening an interconnecting valve between the 50-mL, high-pressure cell and the 10-mL injection vessel. Hydrogen reduction of Pd(hfa)<sub>2</sub> was performed at 200 atmospheres and 50

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± 5 °C. After about 2 hours, Pd was successfully deposited into HDPE granules or PFA rings. The yellowish color caused by Pd(hfa)<sub>2</sub> became dark gray due to Pd metal particle formation as seen in FIG. 4A. A piece of the PFA with Pd nanoparticles was cut in half for observation. The whole cross section (width 1 mm) also was dark gray in color indicating that the Pd precursor penetrated deep into the whole PFA ring in supercritical CO<sub>2</sub> and deposited uniformly in the plastic as metal nanoparticles. FIG. 5 shows a TEM micrograph of the Pd nanoparticles deposited in HDPE. The method for TEM sample preparation was identical to that reported in the literature. *Id.* From the TEM micrograph, the size distribution of the metal nanoparticles was estimated to vary from 2 to 10 nm with the largest fraction in the range of 4-5 nm diameter.

For synthesizing Rh nanoparticles, 3.5 mL chloroform was added to enhance the solubility of Rh(acac)<sub>3</sub> in supercritical CO<sub>2</sub>. In addition, 10 mg of Pd(hfa)<sub>2</sub> also was added as a catalyst for hydrogen reduction of Rh(acac)<sub>3</sub>. The Rh nanoparticle depositions in HDPE granule and PFA ring were performed at 110 and 150 °C, respectively. The plastic-supported, metal nanoparticles are very stable in air. No obvious agglomeration of the metal nanoparticles in the plastic materials was observed even after 3 months of storage in our laboratory based on TEM micrographs.

Newly prepared plastic stabilized Pd and Rh catalysts must be washed thoroughly in supercritical CO<sub>2</sub> to remove possible byproducts produced from the reduction process. Plastic catalysts may be washed repeatedly with neat supercritical CO<sub>2</sub> at 100 atmospheres and 50 °C repeatedly until the byproducts [hexafluoroacetylacetone from Pd(hfa)<sub>2</sub> and acetylacetone from Rh(acac)<sub>3</sub>] are no longer detectable from the trapped solution.

## EXAMPLE 2

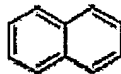
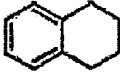




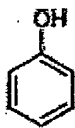


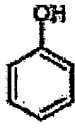
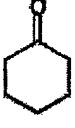

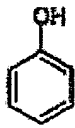
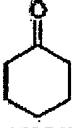


Olefins, arenes and nitro compounds were hydrogenated using the plastic-supported Pd or Rh nanoparticles prepared according to the procedure of Example 1.

The plastic catalyst (4.5 g PFA or 3.0 g HDPE) and a starting material (the amounts are shown in Table 1, below) were placed in a 10-mL, high-pressure stainless cell. The amounts of Pd and Rh in the PFA or HDPE were estimated to be 0.015-0.022 mmol based on the weight difference before and after deposition of the metal precursors in the plastic. The stainless cell was heated to a desired reaction temperature (e.g. 50 °C) in an oven. Hydrogen gas was flowed through the whole system to purge air and then was pressurized to 10 atmospheres. Finally the reactor was pressurized by 100 atmospheres of CO<sub>2</sub> to allow the starting material to dissolve in the CO<sub>2</sub> phase and for the hydrogenation reaction to occur. After a reaction time of 10-60 minutes, the reaction products were collected in a

$\text{CDCl}_3$  solution by the RESS technique for NMR measurements using a 300 MHz NMR spectrometer (BRUKER AMX 300). The results of arene hydrogenation using the plastic supported Pd or Rh nanoparticles as catalysts are summarized in Table 2.

5

**Table 2**  
Hydrogenation of arenes using plastic-supported metal nanoparticles

Metal	Plastic	Starting material	$T/^\circ\text{C}$	$t/\text{min}$	Product (Conversion)
Pd	HDPE	 20 mg (0.15 mmol)	50	15	 (~100%)
Rh	PFA	 15 $\mu\text{L}$ (0.17 mmol)	50	10	 (>99%)
Pd	PFA	 15 $\mu\text{L}$ (0.17 mmol)	50	60	 (86%)
Pd	HDPE	 15 mg (0.16 mmol)	50	60	  (78%) (6%)
Pd	PFA	 15 mg (0.16 mmol)	50	50	  (62%) (38%)
Rh	PFA	 15 mg (0.16 mmol)	50	20	   (60%) (33%) (3%)

10

Using polymer-stabilized, Pd nanoparticles as catalysts (in HDPE granule or in PFA ring), the hydrogenations of arenes proceeds rapidly even at 50  $^\circ\text{C}$ . Hydrogenation of naphthalene to form tetralin was completed within 15 minutes. In order to examine the recyclability of the plastic-supported metal nanoparticles, the hydrogenation of naphthalene using the HDPE supported Pd nanoparticle catalyst was repeated 10 times under the same

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conditions. The conversion of naphthalene to tetralin was always > 99 % and did not show an obvious decrease in hydrogenation efficiency. The fine structures of the plastic are effective for preventing diffusion and agglomeration of the nanoparticles in the plastic structures. On the other hand, the arenes can diffuse smoothly in the swelled plastic structures and can contact nanoparticles because of the extremely small hydrodynamic diameter compared with that of nanoparticles. The plastic-stabilized Rh nanoparticles are more effective than the Pd nanoparticles for catalytic hydrogenation of arenes. The hydrogenation of benzene to cyclohexane using the PFA stabilized Rh nanoparticles was almost completed (99%) within 10 minutes at 50 °C with 10 atmospheres H<sub>2</sub> and 100 atmospheres CO<sub>2</sub>. Using PFA-stabilized Pd nanoparticles under the same reaction conditions, benzene was converted to cyclohexane (86%) after 60 minutes.

FIG. 6 is an NMR spectrum typical of the reaction products found in the trap solution after hydrogenation of benzene using the Rh catalyst in supercritical CO<sub>2</sub>. The only major peaks found in the NMR spectrum are cyclohexane (1.4 ppm) and chloroform from CDCl<sub>3</sub> (7.2 ppm). Two very small peaks at 1.5 ppm and 7.3 ppm are due to H<sub>2</sub>O and the starting material benzene (< 1%), respectively. This result clearly shows that the product can be separated from the plastic catalyst by rapid expansion of CO<sub>2</sub>. Despite repeated use of the same Rh catalyst throughout these trials for hydrogenation of benzene (to determine the hydrogenation speed and to check the reproducibility), the PFA-supported Rh nanoparticles did not show any observable changes in catalytic activity. The Rh nanoparticles are also more effective than Pd for hydrogenation of phenol to cyclohexanone (major) and cyclohexanol (minor).

The hydrogenation of olefin and nitro compounds also was tested using PFA-supported Pd nanoparticles. 4-methoxy cinnamic acid (15 mg) was converted to 4-methoxy hydrocinnamic acid (>98%) in 5 minutes at 50 °C with 10 atmospheres of H<sub>2</sub> and 100 atmospheres of CO<sub>2</sub>. Nitrobenzene (15 µL) was converted to aniline (>98%) with minor products (<2%) cyclohexyl amine and cyclohexane in 5 minutes under the same conditions in supercritical CO<sub>2</sub>.

### EXAMPLE 3

Pd and Rh nanoparticles were deposited into two types of commercial plastics in supercritical CO<sub>2</sub>. One type was high density polyethylene (HDPE) granule with approximately 3 mm in diameter obtained from Goodfellow (Berwyn, PA). Another type was perfluoroalkyl-tetrafluoroethylene copolymer (PFA) tubes with 6 mm outer diameter obtained from Fisher (Pittsburgh, PA). The PFA tube was sliced to rings with 1 mm width

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for metal deposition experiments. In a previous study, Watkins and McCarthy synthesized polymer/Pt nanocomposite in supercritical CO<sub>2</sub>.

The reactor system used for synthesis of Pd and Rh nanoparticles in plastics is illustrated in FIG. 1. The plastic materials (PFA 30 g or HDPE 23 g) were placed in a 50 mL volume stainless steel vessel. Palladium (II) hexafluoroacetylacetonate [Pd(hfa)<sub>2</sub>] and rhodium (III) acetylacetonate [Rh(acac)<sub>3</sub>], purchased from Aldrich, were used as precursors for Pd and Rh nanoparticles, respectively. 250 mg of the precursor [Pd(hfa)<sub>2</sub>: 0.48 mmol or Rh(acac)<sub>3</sub>: 0.62 mmol] were added to the 50-mL cell. The 50-mL cell was preheated to a deposition temperature (e.g. 50 °C for Pd) in an oven. After reaching the desired temperature, neat CO<sub>2</sub> (Instrument grade, Oxarc, Spokane WA) at 80 atmospheres was introduced into the 50-mL cell to dissolve the Pd or Rh precursor. The instrument-grade CO<sub>2</sub> was metered and pressurized by an ISCO syringe pump (model 260D). An injection vessel (10 mL volume), connected with the 50-mL cell by 1/16" tubing with an interconnecting valve, was pressurized with 10 atmospheres hydrogen (4.1 mmol; Oxarc, Spokane WA) after purging ambient air with hydrogen. Neat CO<sub>2</sub> was introduced into the injection vessel to mix with the hydrogen at a total pressure of 200 atmospheres. By opening the interconnecting valve between the 50-mL, high-pressure cell and the 10-mL injection vessel, the CO<sub>2</sub>-H<sub>2</sub> mixture was injected into the 50-mL high-pressure cell with the aid of the pressure difference. The hydrogen reduction of Pd(hfa)<sub>2</sub> was performed at 200 atmospheres and 50 °C. The reduction and metal deposition process required about 3 hours for the best result. For deposition of Rh nanoparticles, 250 mg of Rh(acac)<sub>3</sub> was dissolved in 3.5 mL of chloroform together with 10 mg of Pd(hfa)<sub>2</sub>. The Pd(II) complex was added to serve as a catalyst for hydrogen reduction of Rh(III) in supercritical CO<sub>2</sub>. The chloroform worked as a modifier for enhancing the solubility of Rh(acac)<sub>3</sub> in supercritical CO<sub>2</sub>. The depositions of Rh nanoparticles into HDPE and PFA were performed at 110 °C and 150 °C, respectively. Newly prepared, plastic stabilized Pd and Rh nanoparticles were cleaned with neat CO<sub>2</sub> at 150 atmospheres at least 5 times before use in catalytic hydrodechlorination in order to remove byproducts from the synthesis process (e.g. Hexafluoroacetylacetone and acetylacetone)

After the synthesis process, the color of Pd-deposited PFA was dark gray from the surface to the interior indicative of uniform distribution of the metal nanoparticles in the plastic materials. FIG. 4 shows an optical image of HDPE granules with Rh(acac)<sub>3</sub> or Rh nanoparticles. The HDPE granules with Rh(acac)<sub>3</sub> were prepared as described herein, but the reaction system was depressurized before hydrogen reduction of Rh(acac)<sub>3</sub>. As seen in the image, the orange color caused by Rh(acac)<sub>3</sub> changed to blackish indicative of formation






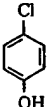

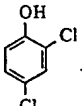

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of Rh nanoparticles. A TEM micrograph of microtomed HDPE with Rh nanoparticles (FIG. 5) reveals that the diameters of the deposited Rh nanoparticles vary from 2 to 10 nm with the largest fraction in the range of 4-5 nm. The Pd and Rh nanoparticles stabilized in these plastics were stable in air and no obvious agglomeration of the metal nanoparticles was  
5 observed based on TEM micrographs after storage for 1 year.

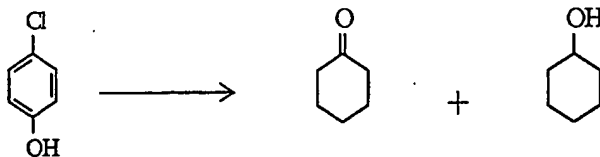
#### EXAMPLE 4

This example describes one embodiment of a process for hydrodechlorination of chlorinated aromatic compounds, such as chlorinated benzenes or biphenyls. The high-  
10 pressure reaction system for hydrodechlorination experiments is illustrated in FIG. 2. The plastic catalysts (4.5 g PFA with 0.036-0.051 wt % of Pd and Rh nanoparticles or 3.0 g HDPE with 0.053-0.077 wt % of Pd and Rh nanoparticles) were placed in a stainless steel chamber (10 mL volume) together with a chlorinated benzene (the amounts are shown in Table 3). After closing the reaction cell, hydrogen gas was flowed through the whole  
15 system to purge ambient air and then the cell was pressurized to 10 atmospheres with hydrogen. After the stainless cell was heated to 50 °C in an oven, 100 atmospheres of CO<sub>2</sub> was introduced into the cell for hydrodechlorination to take place. The reaction products were collected in CDCl<sub>3</sub> using the RESS (rapid expansion of supercritical solutions) technique. Hydrodechlorination results catalyzed by Pd and Rh nanoparticles stabilized in  
20 HDPE and PFA (Pd-HDPE, Pd-PFA and Rh-PFA) are provided in Table 3.

Table 3

Chlorinated benzenes	Catalyst	Time (min.)	Products (conversion %)					
			Total					
 ( $1.2 \times 10^{-4}$ mol)	Pd-PFA	15	100	72	14	7	7	0
	Pd-HDPE	30	100	83	16	0	1	0
 ( $1.5 \times 10^{-4}$ mol)	Pd-PFA	60	100	0	0	0	90	10
	Pd-PFA	30	100	0	0	0	43	57
 ( $0.9 \times 10^{-4}$ mol)	Pd-PFA	70	97	40	48	0	9	0
	Rh-PFA	60	41	7	19	0	15	0
 ( $1.9 \times 10^{-4}$ mol)	Pd-PFA	50	100	62	38	0	0	0
	Pd-HDPE	60	84	78	6	0	0	0

The Pd nanoparticles stabilized in both HDPE and PFA were effective for removing chlorine from *p*-chlorophenol. With 10 atmospheres of H<sub>2</sub> in supercritical CO<sub>2</sub> at 100 atmospheres, hydrodechlorination of *p*-chlorophenol was virtually complete in 15 or 30 minutes using Pd-PFA or Pd-HDPE as the catalyst, respectively. The main products were cyclohexanone and cyclohexanol for both catalysts indicating that catalytic hydrogenation of phenol with the Pd nanoparticles took place following the hydrodechlorination.



- 10 A mixture of cyclohexanone and cyclohexanol is well known as KA oil with an annual production exceeding 5 million tons. O. Fukuda, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.* 42 (2001) 3479-3481. KA oil is an important starting material for Nylon-6 and Nylon-66

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via formations of  $\epsilon$ -caprolactam and adipic acid, respectively. Hydrogenations of phenol using the Pd-PFA or the Pd-HDPE catalyst were tested under the same experimental conditions, and the results also are shown in Table 2. Again, the products of hydrogenation of phenol were cyclohexanone and cyclohexanol but the reaction was slow. Comparing this result with that observed in the *p*-chlorophenol case, the hydrogenation of the phenol portion was facilitated by a chlorine substitution effect. The dechlorination of chlorobenzene was complete within 30 minutes in supercritical CO<sub>2</sub> at 50 °C and 100 atmospheres. Catalytic hydrogenation of benzene to cyclohexane with the Pd nanoparticles also was observed after the dechlorination was completed.

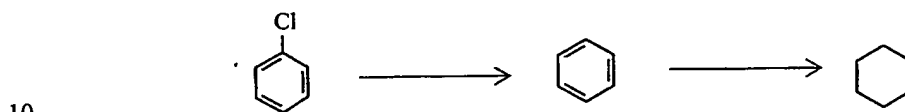


FIG. 7 shows an NMR spectrum of the products collected in CDCl<sub>3</sub>. Only three peaks due to benzene, cyclohexane and CDCl<sub>3</sub> were observed in the NMR spectrum. The result indicates successful separation of the products from the catalysts and the solvent by expansion of supercritical CO<sub>2</sub>.

15 2,4-Dichlorophenol is a high-volume feed stock chemical used in pharmaceuticals and herbicides. G. Yuan, M. A. Keane, Catal. Today 88 (2003) 27-36. Dechlorination of 2,4-dichlorophenol with Pd-PFA catalyst was also studied, and the results are shown in Table 1 and FIG. 8. The amount of 2,4-dichlorophenol decreased linearly with time and virtually disappeared at 70 minutes. The major products were cyclohexanol and cyclohexanone similar to the results observed for the *p*-chlorophenol system.



The conversion to cyclohexanone reached 30% at the first 30 minutes and did not increase much after extended reaction times. On the other hand, the conversion to cyclohexanol was very small (less than 10 %) at the first 20 minutes and almost linearly increased after that.

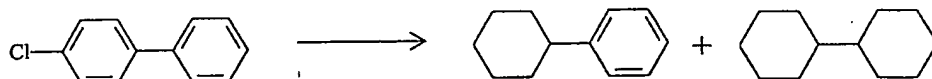
25 The conversion profile of these two compounds suggests that 2,4-dichlorophenol was hydrogenated to cyclohexanol through formation of cyclohexanone. Rh nanoparticles stabilized in water-in-CO<sub>2</sub> microemulsions were reported to be very effective for catalytic hydrogenations of olefins and arenes. The hydrodechlorination of 2,4-dichlorophenol was carried out using Rh-PFA catalyst. Comparing the result to using Pd-PFA, though the

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conversion to benzene was higher using the Rh catalyst, the net dechlorination speed was much slower.

The Pd-PFA and Rh-PFA catalysts were used for hydrodechlorination reactions repeatedly to examine the recyclability. If the catalysts were cleaned with neat CO<sub>2</sub> immediately after use, their catalytic capability remained the same even after a dozen times of repeated uses for this research.

Hydrodechlorination of 4-chlorobiphenyl (BZ# 3) catalyzed by Pd-PFA was carried out using a different reactor system shown in FIG. 3, which consists of two stainless steel vessels, one is a 15 mL volume reactor with the Pd catalysts (7g Pd-PFA) and the other is a 40 mL volume vessel for storage of reactant (10 mg of 4-chlorobiphenyl). Hydrogen was flowed through both of the stainless steel chambers to purge ambient air first and then pressurized to 10 atmospheres. Since the solubility of 4-chlorobiphenyl in CO<sub>2</sub> increased at temperatures above its melting point (76-77 °C), the stainless vessels were heated to 80 °C in an oven. After reaching at 80 °C, CO<sub>2</sub> at 150 atmospheres was introduced into the storage vessel to dissolve the 4-chlorobiphenyl and hydrogen. The CO<sub>2</sub> containing 4-chlorobiphenyl and hydrogen was then injected into the reactor by opening an interconnecting valve between the reactor and the storage vessel. The reaction products were collected in a CDCl<sub>3</sub> solution after 30 minutes of reaction time. The injection and collection processes were repeated continuously 5 times to introduce most of the 4-chlorobiphenyl into the reactor for hydrodechlorination. Based on the NMR spectrum of the products collected in the CDCl<sub>3</sub> solution as shown in FIG. 9A, 4-chlorobiphenyl passing through the reactor with the Pd-PFA catalysts was successfully dechlorinated (~ 100 %). The products were 85% dicyclohexyl, 14% cyclohexyl benzene and < 1 % biphenyl.



The NMR spectrum showed a H<sub>2</sub>O peak besides the three products described above. The water was contained in the chlorobiphenyl reagent as an impurity.

Chlorinated benzenes with one or two chlorine substituents and chlorobiphenyl can be effectively dechlorinated by hydrogen in supercritical CO<sub>2</sub> using polymer-stabilized Pd or Rh nanoparticles. The polymer reagents can be reused without losing the high catalytic activity inherent by nanometer-sized particles. The factors for deactivation, such as leaching of metal particles from support, agglomeration and sintering, are eliminated in the presently disclosed system, because of the unique polymeric matrix environment. The poisoning of Pd and Rh particle surfaces with HCl was not observed. Using the disclosed embodiments, nanoparticle reagents may be tailored depending on purposes and reactions

by choosing a wide variety of polymer support materials with different shapes and sizes. The chemical properties of polymer materials may affect mechanisms of catalytic chemical reactions. Since swelling of polymer structures in CO<sub>2</sub> facilitates contacting nanoparticles embedded in polymers, the reactions may be carried out in supercritical fluids, such as  
5 supercritical CO<sub>2</sub>. Supercritical CO<sub>2</sub> can be used as a green solvent for extracting toxic compounds from natural samples. Therefore, a combination of supercritical fluid extraction and a catalytic reaction system utilizing the plastic catalysts may have great advantages over other processes of destroying toxic chlorinated compounds from environmental samples.

Polymer-supported metal nanoparticles may have great advantages over other  
10 nanoparticle reagents in chemical synthesis and manufacturing processes, because of their stability, recyclability, easy handling and separation of products. The technique can be applied to other metal reagents and different polymers than disclosed herein as examples. Since various forms of high temperature polymers, such as polyimide, polytetrafluoroethylene and polybenzimidazole, are commercially available, the polymer-  
15 supported metal nanoparticles may be used for high temperature reactions.

The disclosed technology was described with reference to specific embodiments. The scope of the invention should not be limited to the particular embodiments described.